Properties of Organo-Clay/Natural Rubber Nanocomposites: Effects of Organophilic Modifiers

Jana Hrachová,[1] Peter Komadel,[1] Daniela Jochec-Mošková,[2] Juraj Krajči,[2] Ivica Janigová,[2] Miroslav Šlouf,[3] Ivan Chodák[2]

[1]Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-845 36 Bratislava, Slovakia
[2]Polymer Institute, Slovak Academy of Sciences, SK-845 41 Bratislava, Slovakia
[3]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 160 06 Prague, Czech Republic
Correspondence to: I. Chodák (E-mail: upolchiv@savba.sk)

ABSTRACT: The effect of various modifiers on the structure and properties of clay/natural rubber nanocomposites are investigated with the aim to evaluate the effect of size and structure of the modifier. Nanocomposites are prepared by melt intercalation method. Mechanical properties of the cured rubber containing nanoclay are compared with the reference compound without the filler. No improvement of mechanical properties is observed for small organic cations; however, stress and strain at break of clay/rubber nanocomposites increase with rising number of octyl chains in the interlayer spaces of organo-clays. Concerning organo-cations with the same number of carbon atoms, more effective are the modifiers with several shorter carbon chains compared to those with one long chain. The composites exhibit hybrid structure of nanocomposite and microcomposite as revealed by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The details of the structure are supported by DMTA and hysteresis measurements. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Among polymer-based nanocomposites, recently rubber matrices attract a particular interest. Besides number of interesting articles, several good reviews and monographies have appeared,[1-4] giving comprehensive overview of the current status of the knowledge in this area. The main reason for the rising interest in rubber nanocomposites consists in substantial changes of properties such as reinforcing concerning mechanical behavior,[5] higher flame resistance,[6] improved barrier properties,[7] similar to the effect of nanofillers in other polymers, but also several rather unique properties are described advantageous especially for elastomeric matrix such as fracture toughness as well as abrasion and tear resistance.[8,9]

In the scientific literature, a vast number of information on rubber nanocomposites can be found dealing with various aspects of the topic. It is generally accepted that if clay-based nanocomposites with good physical properties are to be formed,

good contact between hydrophilic filler surface and hydrophobic polymer must be achieved accompanied by an increase in polymer-filler interactions. These interactions may be of physical, physicochemical, and chemical nature and they depend on compatibility between the filler surface and the polymer matrix, related to number of factors, such as adhesion between the phases, affinity of the two different surfaces and surface area of the filler. The surface of layered silicates in their pristine state is hydrophilic and only compatible with hydrophilic polymers, such as poly(ethylene oxide) or poly(vinyl alcohol). To render them compatible with hydrophobic polymers, the alkali counter-ions must be substituted by an appropriate cationic-organic surfactant. Alkylammonium ions are mostly used,[10–15] although other "onium" salts can be used, such as sulfonium and phosphonium. The introduction of organic cations results in a decrease of the surface energy of the silicate surface, leads to a change in the nature of the clay from hydrophilic to hydrophobic and improves wetting by the polymer matrix. Sometimes,

the alkylammonium cations may even provide functional groups that can react with the polymer or initiate polymerization of monomers.[16]

Various methods of preparation of elastomer-based nanocomposites[5,17,18] lead to various degree of intercalation/exfoliation and even to different structures; e.g., a formation of peculiar skeleton-type structure by latex mixing was described.[4] The influence of vulcanization kinetics by the presence of nanofillers[19] is discussed as well. Investigating various nanofillers such as modified and unmodified montmorillonite (MMT), sepiolite, carbon nanofiber, and carbon black, it was found that the effect on vulcanization differs substantially, e.g., in a presence of organo-modified nanoclay (OMMT), optimum cure time was reduced whereas the presence of carbon nanofiber resulted in a slower vulcanization.[20] For rubber nanocomposites also, nanokaolin and precipitated silica are frequently used as nanofillers.[21] It should be mentioned that besides sulfur vulcanization of rubber nanocomposites other curing systems have been reported such as peroxide[22] and electron beam irradiation.[23]

The significant reinforcing effects observed for exfoliated clay-based nanocomposites with polymer matrix are attributed to the highly anisotropic nature of silicate layers. Indeed, with a few exceptions, the majority of the polymer nanocomposites reported in the literature was found to have intercalated or mixed intercalated-exfoliated nanostructures. Intercalation or exfoliation of smectite can currently be monitored most exactly by atomic force microscopy (AFM), transmission electron microscopy (TEM), and X-ray diffraction analysis, especially small angle X-ray scattering (SAXS), as has been described in numerous recently published studies of clay-rubber nanocomposites.[24–27] New method was developed for the characterization of morphology development and kinetics of nanoclay distribution in hydrogenated acrylonitrile butadiene rubber (HNBR)/natural rubber (NR) blends based on the measurement of electrical conductivity during the mixing process.[28] It was suggested that the online measured electrical conductivity of rubber-clay mixtures, which originates from the release of the ionic surfactant from the nanoclay galleries during the mixing process depends on two factors: the phase specific localization of nanoclay and the change of the blend morphology.

Concerning mechanical properties, the increase in tensile strength and modulus are reported together with the increase in elongation at break indicating an important reinforcing effect in many cases. The mechanical properties are frequently investigated also in dynamic mode (dynamic mechanical properties)[29] and hysteresis behavior is also described.[30] Usually, a decrease in tan δ intensity and increase of glass transition temperature, T_g, is observed after addition of nanofillers interpreted in terms of confinement of the macromolecular segments into the organo-clay nanolayers and the strong interaction between the filler and rubber matrix.[17] The effect is selective to certain extent because for NR/BR blends, the shift of loss factor peak (tan δ) to higher temperatures was observed to be more pronounced for the NR phase compared with BR.

Another important item related to rubber nanocomposites is the increase in the resistance to crack growth as a result of OMMT addition to NR.[31] The study on the viscoelastic properties by dynamic mechanical analysis indicated that NR filled with 10 phr OMMT had the largest contribution to tearing energy attributed to the viscoelastic dissipation in the viscoelastic region in front of the crack tip. This effect is supposed to be partially related to changes in the effect of strain-induced crystallization, which is also influenced by a presence of nanoclay. It was shown that the clay initiates the changes in the strain-induced crystallization behavior of natural rubber and induces a dual crystallization mechanism as a result of the orientation of clay layers during deformation.[32] The entropy change required for the onset of the strain-induced crystallization of the clay filled rubber is composed of the entropy reduction because of both the rubber-filler interactions and the stretching of rubber macromolecules.[32]

This work is a part of complex investigation of one series of organo-clays and their use in clay-polymer nanocomposites.[33,34] Previous studies have shown that small cations 1C8 (octylammonium), C10 (benzyltrimethylammonium), and C12 (4-vinyl-benzyl-trimethylammonium) saturated only 56–76% of the cation exchange capacity (CEC) in the organo-clays prepared from sodium MMT (Na-MMT); the amounts of 2C8 (dioctylammonium), 4C8 (tetraoctylammonium), 1C16 (hexadecylammonium), and 2C16 (dihexadecyldimethylammonium) were close to the full exchange (100 % CEC), and the highest organo-cation content of ~40 mass% or 150% of CEC of Na-MMT was found for 3C8 (trioctylammonium) cation.[33] It should be stressed that values exceeding 100% indicate that the replacement of inorganic with organic cations cannot be considered to be a simple ion exchange, but sorption of additional cations on the clay particles occurs. Great potential of the near infrared (NIR) spectroscopy for characterization of organically modified clay minerals is discussed in detail in Ref. 34; the water content in this series decreased with the size of organic cation, indicating the increase of the MMT surface hydrophobicity. This is a promising feature for the interactions of the modified MMTs with the polymers.
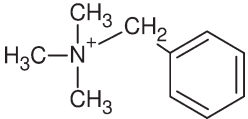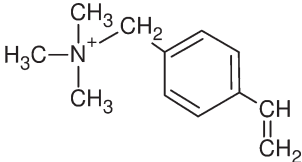
The aim of this work is to investigate the effect of various modifiers on the structure and properties of clay/rubber nanocomposites. The modifiers have similar hydrophobicity and the difference consists in size of the modifier affecting the interlayer distance of the filler before mixing in the rubber matrix.

EXPERIMENTAL

MMT, <2 μm fraction separated from Jelšový Potok bentonite (Slovakia), was saturated with Na$^+$ cations (Na-MMT) and subsequently treated with different organic surfactants (Table I). Details of preparation and characterization of the organo-clays appear in Ref. 33.

Natural rubber SMR-20 (NR; Malaysia, supplied by Vegum, Slovakia) was used as the elastomeric matrix. The blends were prepared by mixing natural rubber with the filler and all the vulcanization ingredients except sulfur namely natural rubber, organo-clay (3 phr—parts per hundred parts of rubber), zinc oxide (5 phr, Slovzink, Slovakia), stearic acid (2 phr, supplied by Fluka), Sulfenax CBS/MG (3.5 phr, Istrochem, Slovakia), in a

Table I. Structures of Organo-Cations Used for Preparation of Organo-Clays from Na-MMT

C10: Benzyltrimethylammonium	C12: 4-vinylbenzyl-trimethylammonium
1C8: Octylammonium	2C8: Dioctylammonium
3C8: Trioctylammonium	4C8: Tetraoctylammonium
1C16: Hexadecylammonium	2C16: Dihexadecyldimethylammonium

30 ml mixing chamber of a Brabender Plasticorder PLE 331 at 70°C for 14 min at the mixing speed 30 rpm. Sulfur (3.5 phr, Siarkopol, Poland) was added in a separate second step on a roll mill. Organo-clays were dried before mixing for 3 h at 100°C and then fed to the chamber. Slabs were obtained by compression molding of the mixed nanocomposite using a laboratory press Fontijne 200 (Fontijne, The Netherlands) at 150°C for 35 min (optimum vulcanization time determined by rheometry) under 22.5 kN·cm^{-2}. Seven dogbone specimens with a working area of 35 mm × 3.6 mm × 1 mm were mechanically punched from each vulcanized slab using a special shaped knife.

Mechanical properties were measured according to ISO 37 at room temperature using an Instron 4301 universal testing machine (Instron, UK) at deformation rate (crosshead speed) 50 mm·min^{-1}. Tensile strength, elongation at break, and modulus at 100% elongation (M100) were determined. All measurements were made on 5–7 dogbone specimens for each sample, and the values were averaged. Hysteresis measurements were performed using the same instrument and specimens of the same size, in deformation loop between 0 and 40% deformation at deformation rate 10%/min.

X-ray powder diffraction (XRD) data were collected for Na-MMT and all the organo-clays on a D8 Advance diffractometer (Bruker AXS, Germany) using Cu-Kα (40 kV, 40 mA, λ = 1.541 78 Å) radiation and a secondary beam graphite monochromator. Diffraction patterns were collected in the 2 to 80° 2θ range in steps of 0.02° 2θ and 2 s counting time per step. XRD profiles for nanocomposites containing 3 phr of the filler were recorded on a diffractometer D8 Discover (Bruker AXS, Germany) using Cu-Kα radiation, 40 kV/300 mA, 2θ range in steps of 0.05° 2θ, 1 s counting time per step).

The morphology of clay/rubber nanocomposites was studied by TEM. The cryo-ultramicrotomed sections (Ultracut UCT, Leica) of the samples were investigated using a TEM microscope JEM 200CX (JEOL) microscope (80 kV, bright field imaging).

Additional data were obtained also from scanning electron microscopy (SEM) using a CARL ZEISS-EVO 40 microscope. All samples for SEM observation were coated with gold before imaging. Dynamic mechanical analysis was done on slabs of dimensions 20 mm length, 6 mm width, and 0.5 mm thickness on instrument Q800 (TA Instruments) in temperature range −100°C to +140°C at heating rate 2°C/min, 64 μm amplitude and 10 Hz frequency.

RESULTS AND DISCUSSION

The organo-clays were prepared by using organic modifiers with different structure and length of alkylammonium chains (Table I). The base of C10 and C12 modifiers is the benzene ring, the only difference between the two being is the presence of a vinyl group in C12. The idea behind modification by vinyl-trimethyl-benzylamine consists in the introduction of double bonds and their possible chemical interactions with the matrix during vulcanization. The other set of modifiers was selected considering the differences in size of the cation and the length of the alkyl chains. The set 1C8, 2C8, 3C8, and 4C8 as well as 1C16 and 2C16 will reveal the effect of molecular mass of the cation. The positive effect on the hydrophobicity of organo-clays together with the ability of rubber chains to intercalate between the silicate layers should play a role. The comparison of the pairs 2C8/1C16 and 4C8/2C16 will reveal the effect of carbon chain length for the cations of the same molecular mass.
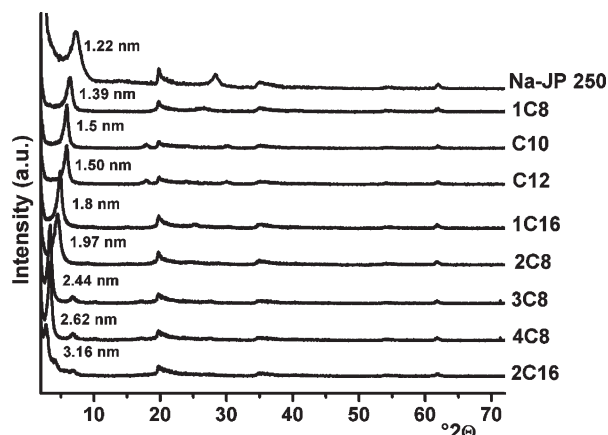
Figure 1. XRD patterns of initial sample Na-MMT and its organically modified forms.

Table II. Mechanical Properties (Strain at Break ε, Stress at Break σ, Modulus 100–M100) and the Ratio ε/σ of Nanocomposites Based on Natural Rubber Matrix (NR) and 3 phr of Organo-Clays (C10–2C16)

Type of blend	ε (%)	σ (MPa)	M 100 (MPa)	σ/ε
NR	115 ± 8	1.6 ± 0.1	1.5 ± 0.1	0.014
NR + C10	87 ± 5	1.5 ± 0.1	1.5 ± 0.1	0.017
NR + C12	85 ± 5	1.5 ± 0.1	1.5 ± 0.1	0.018
NR + 1C8	89 ± 16	1.5 ± 0.1	1.5 ± 0.2	0.017
NR + 2C8	98 ± 3	1.7 ± 0.1	1.7 ± 0.1	0.017
NR + 3C8	138 ± 11	2.5 ± 0.2	2.1 ± 0.1	0.018
NR + 4C8	162 ± 29	3.0 ± 0.9	2.1 ± 0.2	0.019
NR + 1C16	89 ± 7	1.5 ± 0.1	1.6 ± 0.1	0.017
NR + 2C16	159 ± 6	3.0 ± 0.1	2.3 ± 0.1	0.019

When the inorganic exchangeable cations are replaced by alkylammonium cations, the clay mineral surfaces not only become more hydrophobic and compatible with polymers but also the interlayer spaces expand and facilitate the intercalation of polymer chains. The XRD patterns of Na-MMT and organo-clays are shown in Figure 1 including the interlayer distances. The basal spacings of organo-modified MMTs increase with the size and structure of the organo-cations. The XRD pattern of the starting material Na-MMT shows a symmetric diffraction with $d_{001} = 1.22$ nm, a value typical for dried Na-MMTs. The diffraction with $d_{001} = 3.16$ nm for 2C16 is the highest among all the samples and larger by 2 nm compared with the initial distance separating the layers in Na-MMT. The d_{001} values prove successful intercalation of the organic cations into the interlayer space of Na-MMT promising for successful intercalation of rubber chains.

Table II gathers data of mechanical testing in tensile mode of rubber blends containing 3.0 phr of organo-clay filler. The mechanical properties of the organo-clay/rubber nanocomposites, such as strain at break and stress at break, were impaired compared with the untreated vulcanized natural rubber when the organo-cations with aromatic ring (C10 and C12) or with up to two octyl chains (1C8–2C8) were used for modification of MMT. However, more bulky organo-cations exhibit a larger positive effect on mechanical properties resulting in simultaneous gains in tensile strength, moduli, and elongation (3C8, 4C8, 2C16). The reinforcing effect is presumed to occur because of formation of intercalated or even partly exfoliated organo-silicate layers between rubber chains and their strong mutual interfacial interactions. Stress–strain curves of all composites are shown in the Figure 2. It is seen that the curves are of the same shape differing just by the values of strain and consequently stress. The difference between unfilled NR and the composites filled with OMMTs consists mainly in the steeper shape of the latter. The higher is the reinforcing effect of the filler, the higher are values of both tensile strength and elongation at break. This is demonstrated also by the ratio of stress/strain (Table II), for all composites being the same whereas the value for unfilled NR is smaller.

It was expected that the double bond of the vinyl group in C12 can participate in the curing reaction and may result in

increased interactions between the rubber matrix and the filler on the phase boundaries. The effect was observed for MMT modified with either octadecylamine or oleyl amine, both being hydrocarbon chains of 18 carbon atoms differing only by a presence of one double bond in the middle of the alkyl chain in the latter.[16] The presence of MMT modified with the ligand with the double bond resulted in much higher tensile strength of the rubber-based nanocomposite. However, the mechanical properties observed for the nanocomposite with the filler C12 are close to those of the system with C10, the filler of similar structure but without the highly-reactive vinyl group. This indicates that the double bond in the C12 filler, expected to possibly affect the vulcanization process, was indeed ineffective in curing reaction in natural rubber and did not affect the stress and strain values. The possible reason consists in too short vinyl moiety with the double bond being inaccessible for bonding to the rubber matrix via sulfur links or, perhaps, lowers reactivity of the vinyl group in proximity of the benzene ring.

The reinforcing effect of the organo-modified fillers increases with the rising number of the alkyl chains in the alkylammonium cations 1C8, 2C8, 3C8, 4C8, and 1C16, 2C16. The highest
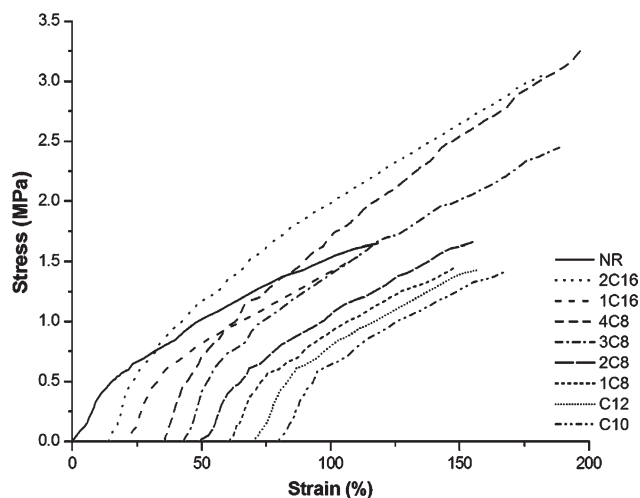

Figure 2. Stress–strain curves of the NR filled with 3 wt % of bentonites modified by various organomodifiers (for identification of the fillers see Table I).

elongation and strength values of all nanocomposites were obtained for those containing 4C8 and 2C16 fillers with the similar molar mass. Cations with carbon atoms divided into more octyl chains seem to be more effective than those with the same amount of carbon atoms in one or two longer hexadecyl chains (2C8 vs. 1C16, 4C8 vs. 2C16). The suitability of the 4C8, 1C16, and 2C16 organo-clays to be used as fillers for polymer nanocomposites was indicated also from data of the rheological measurements of their dispersions, forming gels in benzyl alcohol.[33]

The reinforcing effect depends on relevant parameters of the filler, for example, on the surface modification, particle size, particle shape, and dispersion in the polymer matrix. The organo-clays are expected to be most effective if fully exfoliated and dispersed homogenously rather than if larger microparticles are present in the polymer matrix. The degree of polymer intercalation in MMT layers has been studied by XRD (Figure 3). An increase in interlayer spacing because of the intercalation of the polymer results in a lower-angle shift of the 001 peak, compared with the basal diffraction of the initial organo-clay particles. The broad peak occurring near $6°2\theta$, best visible in the traces of 4C8 and C10 (Figure 3), corresponds to $d_{001} = 1.47$ nm or interlayer distance of ~ 0.5 nm and suggests that a part of the clay mineral layers is separated by roughly 0.5 nm on intercalation with the organo-cations (Figure 1) and possibly with the rubber as well. Organo-clays in nanocomposites with rubber are of partially intercalated layers. The disappearance of the 001 diffraction was not observed for any of the fillers, indicating that full exfoliation had not occurred.

From this point of view, it is a bit surprising that the 4C8 being one of the largest cations used for MMT modification, shows the most intense peak in the XRD of composites. The respective composite exhibits the highest both elongation at break and tensile strength, the same as the material containing 2C16 (Table II), although the XRD records of the both differ significantly. Different structures are confirmed also by TEM where the composite filled with 2C16, compared to all others including the one with 4C8, shows finer structure (Figure 4), smaller inhomogeneities (Figure 5), and higher concentration of nanoparticles, as seen in both Figures 4 and 5. It is suggested that even if the exfoliation proceeds only to a limited extent, extensive intercalation may have similar or even higher reinforcing effect as a result of interconnection of the structure by macromolecules anchored inside the galleries. Natural rubber with rather long chains can be suitable for this kind of structure formation, with one end of the chain anchored inside the filler galleries whereas the other end is available for entanglement formation with bulk of the rubber. Such a structure may be considered as a kind of permanent physical crosslinks within the nanocomposite, although it is difficult to explain the route how this morphology could be formed on purpose.

To confirm intercalation and the homogeneous dispersion of the organo-clays in the nanocomposites, morphological investigations were done using TEM. TEM observation corresponds fully with the data from XRD and with mechanical properties. Two sets of TEM micrographs were selected to demonstrate the
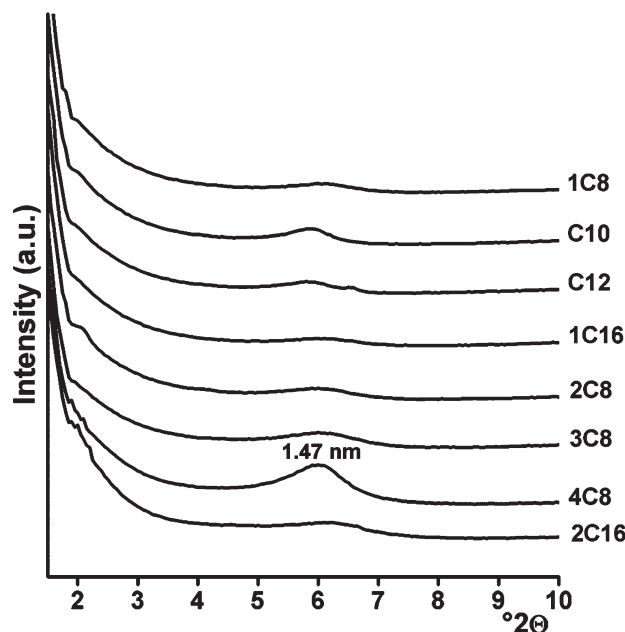

Figure 3. XRD patterns of natural rubber nanocomposites with 3 phr of various organo-clays.

distribution of the filler in Figure 4. The micrographs are shown representing the typical patterns of particle distribution observed through the sample, whereas in Figure 5, the biggest inhomogeneities are seen, as observed in the particular sample. It is quite clear that with rising molar mass of the ligand, the homogeneity of the particle distribution increases, and also the size of filler particles and the number of inhomogeneities decreases. Moreover, for composites filled with MMT modified with the largest ligands the number of small, nanosize particles is much higher compared with those containing MMT modified with smaller ligands. TEM micrographs of nanocomposites filled with 4C8 and 2C16 organo-clays clearly show an intercalated structure, homogeneously dispersed into the rubber matrix. It is worth to mention that the effect of fillers modified with the ligands of the similar molar mass, i.e., 2C16 and 4C8, on all factors discussed above (mechanical properties, XRD, TEM) is very similar, supporting the suggestion that molar mass of the alkyl ligand is much more important than the length of the alkyl chains of the organomodifier of the same chemical nature.

SEM was used to investigate the homogeneity of clay particles dispersion in the rubber matrix. The pictures in Figure 6 show the homogeneity of dispersions on larger scale and support the conclusions made from TEM. Higher amounts of rather large filler particles observed in the mixtures containing organo-clays with short alkyl chains (1C8) or aromatic rings (C10, C12) correspond to their small effect on mechanical properties (Figure 6; 1C8 is only shown as an example). Despite better dispersion resulting in the formation of small particles close to nanosize in composites with fillers with multiple alkyl chains (2C8, 3C8, 4C8, 2C16), the mixing conditions did not allow full exfoliation of all filler particles and some of microsize species were still visible (Figure 6, 4C8 is shown, the others are almost the same).
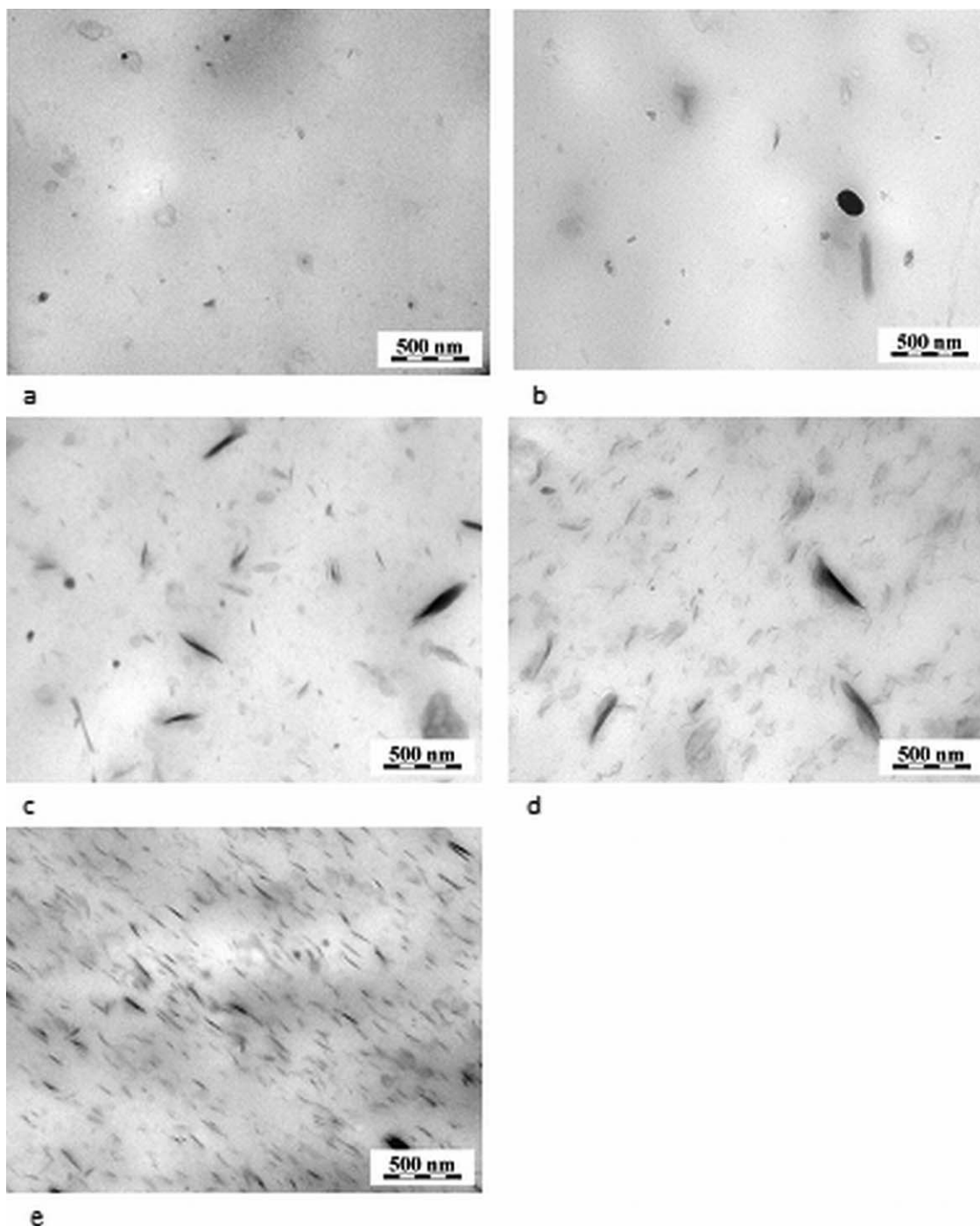
Figure 4. The typical homogeneous filler distribution in the composites of natural rubber with MMT modified with C8 (a), 2C8 (b), 3C8 (c) 4C8 (d), and 2C16 (e).

As said above, according to the XRD records of the modified MMTs (Figure 1), the intergallery spacings broaden with rising size of the modifier molecule. However, under the mixing conditions, the organo-clay particles did not decompose to completely exfoliated structure, even, as seen in SEM images (Figure 6), part of the filler stays in the form of microparticles. Moreover, the XRD patterns of fillers after synthesis show clear effect of the increase in intergallery distance with growing size of the

organomodifier. It is interesting that XRD (Figure 3) shows only one peak for the most fillers, but for the most bulky modifiers (3C8, 4C8, and 2C16), the record consists of one major peak moving to smaller 2θ values with rising size of the modifier molecule and a small peak at around $6°2\theta$ indicating a presence of structure with only small increase of the layer distance or even no intercalation of the modifier within certain parts of the filler. Thus, it is concluded that in the fillers with most
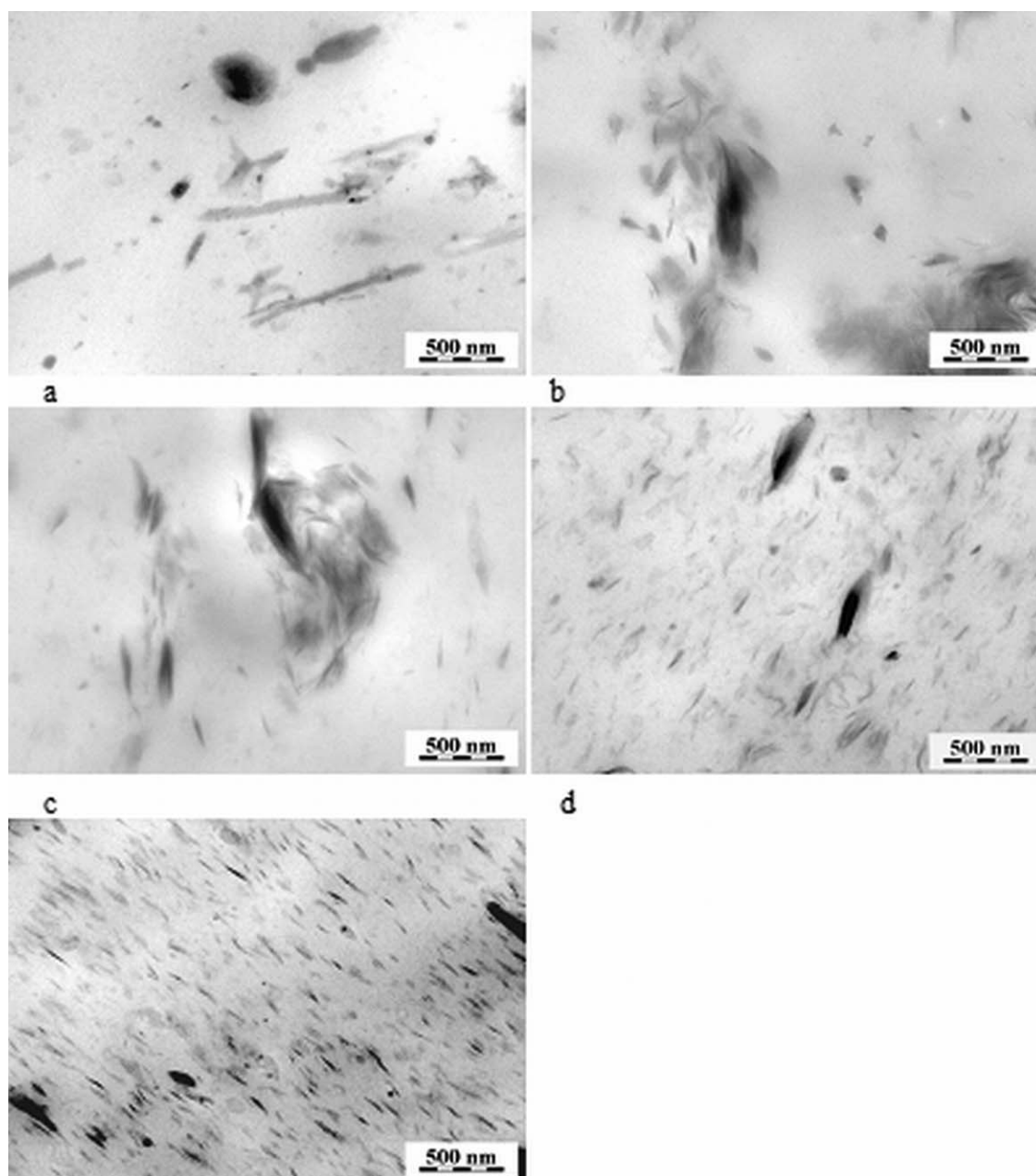
Figure 5. The largest inhomogeneities observed in the composites of natural rubber with MMT modified with C8 (a), 2C8 (b), 3C8 (c), 4C8 (d), and 2C16 (e).

bulky modifiers, the particles with large intergallery distances are present accompanied by particles with d_{001} distributed around 1.47 nm (Figure 3), as can be concluded from the shape of this quite broad diffraction peak. The remnants of these structures explain the appearance of microparticles also in composites containing bentonite with bulky organomodifiers observed by SEM (Figure 6), as well as the peak in the XRD of composite filled with 4C8 modified filler (Figure 3). However, these structures do not interfere with the reinforcing effect of nanoparticles formed in the material, the only influence consists in a decrease of the concentration of exfoliated and intercalated particles, which is important but not crucial considering the

effect on the mechanical properties. Thus the overall reinforcing effect may be lower than expected but still high enough to be considered as significant. This is also why SEM images indicate existence of microcomposites in all materials. These relatively large particles are present in all composites but the overall portion is just a small part of the total content of the OMMT filler, most of the filler having been decomposed to either intercalated structures or exfoliated nanoparticles as indicated by TEM. Similar behavior regarding XRD patterns was observed also by other authors as shown in Ref. 4.

Additional information on the composites properties have been obtained from DMTA. Generally, the presence of nanofiller in
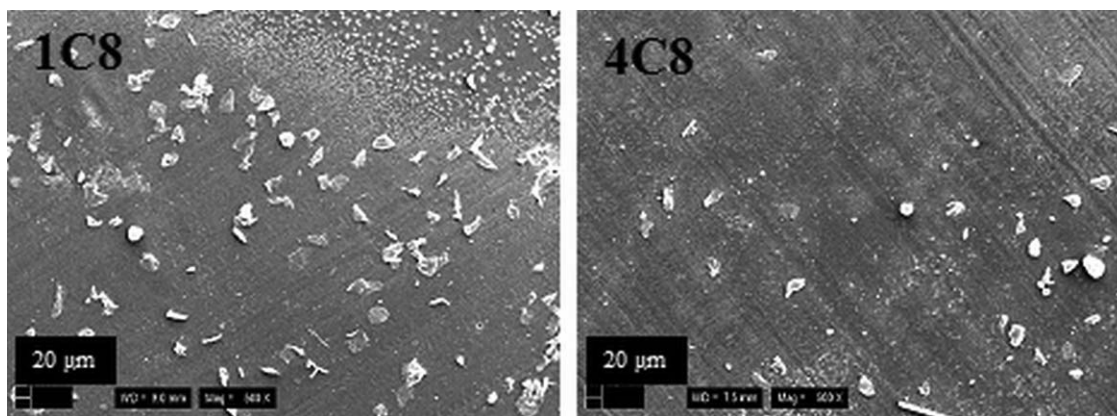
Figure 6. SEM images of rubber nanocomposites containing 3 phr of 1C8 and 4C8 organo-clays.

the composite should result in a decrease of the mobility of polymer chains and consequently to an increase of the glass transition temperature, T_g.[4,17] Indeed, as seen in Table III, this was the case if comparing the OMMT-filled rubber with unfilled natural rubber vulcanizate, however, in fact only marginal changes, if any, were observed when comparing the rubber filled with various OMMTs. Comparison of absolute values of loss angle tan δ height in the peak maximum were somewhat more instructive; an appearance of certain trend could be admitted indicating a decrease in the peak height with growing size of the organomodifier. This seems to be in accordance with a decrease in mobile phase resulting in an increase of reinforcing as a result of higher degree of intercalation/exfoliation; however, the observed effect is rather small so that it is questionable whether it is statistically significant. From DMTA records also more practical values were taken, namely the tan δ values at 0°C, which should correspond to the hysteresis losses relative to the traction of tire on wet surface. It is seen that with rising size of the modifier, the thread with OMMT content should be more resistant to slipping on wet surface.

The results from DMTA were confronted with hysteresis measurement at room temperature. The hysteresis loop was meas-

ured at 10% deformation. The loop has standard shape therefore only the hysteresis loss values are given in Table III. It is seen that the hysteresis losses are higher for composites with OMMT modified with larger modifiers. This result corresponds with the DMTA data.

CONCLUSIONS

Clay/natural rubber nanocomposites were prepared using different organo-modified MMTs and the mechanical properties of rubber were improved by adding even small amounts of organo-clays (3 phr). The results indicate the significant role of the type, structure, and molar mass of organo-cation used for the mechanical properties of rubber/organo-clay nanocomposites. The highest values of modulus 100, stress, and strain at break were obtained for nanocomposites with organo-clays 4C8 and 2C16 with the largest interlayer distances. It was found that organo-cations with the same number of carbon atoms but different structure affect the mechanical behavior of clay/rubber nanocomposites differently. Cations with carbon atoms divided into more alkyl chains are more effective. The composites exhibit hybrid structure of nanocomposite and microcomposite as revealed by XRD, TEM, and SEM. The details of the structure have been supported by DMTA and hysteresis measurements.

Table III. The Effect of 3 wt % of Bentonite Modified by Various Organomodifiers on Dynamic Mechanical Behavior (Glass Transition Temperature, T_g, Intensity of the tan $\boldsymbol{\delta}$ Peak at T_g I tan $\boldsymbol{\delta}$, and at 0°C I tan $\boldsymbol{\delta}$ 0°C) and Hysteresis Losses A for 40% Deformation of the Natural Rubber-Based Composites

Blend	T_g (°C)	I tan δ, au	I tan δ 0°C, au	A
C8	−35.61	1.88	0.090	4.2
C10	−35.02	1.75	0.104	4.2
C12	−36.68	1.88	0.085	5.0
C16	−35.81	1.69	0.096	5.9
2C8	−37.40	1.83	0.092	7.5
3C8	−35.95	1.75	0.090	8.4
4C8	−37.27	1.67	0.115	7.5
2C16	−35.42	1.66	0.120	7.5
NR	−48.0	1.78	0.306	10.9

REFERENCES

1. Thomas, S.; Stephen, R., Eds. Rubber Nanocomposites; Wiley: Singapore, **2010.**

2. Galimberti, M., Ed. Rubber-Clay Nanocomposites. Science, Wiley-VCH: Weinheim, **2011.**

3. Mohammad A.; Simon, G. P. In Polymer Nanocomposites; Mai, Y. W., Yu, Z. Z., Eds.; Woodhead Publ. Ltd., CRC Press LLC: Cambridge, Boca Baton, **2006.**

4. Karger-Kocsis, J.; Wu, C.-M. *Polym. Eng. Sci.* **2004,** *44*, 1083.

5. Sengupta, R.; Chakraborty, S.; Bandyopadhyay, S.; Dasgupta, S.; Mukhopadhyay, R.; Auddy, K.; Deuri, A. S. *Polym. Eng. Sci.* **2007, 1956.**

6. Khanlari, S.; Kokabi, M. J. *Appl. Polym. Sci.* **2011,** *119*, 855.

7. Li, P.; Wang, L.; Song, G.; Yin, L.; Qi, F.; Sun, L. J. *Appl. Polym. Sci.* **2008,** *109*, 3831.

8. Xu, D.; Karger-Kocsis, J. J. *Mater. Sci.* **2010,** *45*, 1293.

9. Zhang, L. Q.; Wang, Y. Z.; Wang, Y. Q.; Sui, Y.; Yu, D. S. J. *Appl. Polym. Sci.* **2000,** *78*, 1873.

10. Hrachová, J.; Komadel, P.; Chodák, I. J. *Mater. Sci.* **2008,** *43*, 2012.

11. Hrachová, J.; Komadel, P.; Chodák, I. *Clays Clay Miner.* **2009,** *57*, 444.

12. Sadhu, S.; Bhowmick, A. K. J. *Mater. Sci.* **2005,** *40*, 1633.

13. Gatos, K. G.; Karger-Kocsis, J. *Polymer* **2005,** *46*, 3069.

14. Arroyo, M.; López-Manchado, M. A.; Valentín, J. L.; Carretero, J. *Compos. Sci. Technol.* **2007,** *67*, 1330.

15. Xidas, P. I.; Triantafyllidis, K. S. *Eur. Polym. J.* **2010,** *46*, 404.

16. Hrachová, J.; Komadel, P.; Janigová, I.; Šlouf, M.; Chodák, I. Polym. Adv. Technol., accepted, Doi: 10.1002/pat.2060.

17. Yuhai, S.; Yuanfang, L.; Demin, J. J. *Appl. Polym. Sci.* **2008,** *107*, 2786.

18. Pramanik, M.; Srivastava, S. K.; Samantaray, B. K.; Bhowmick, A. K. J. *Appl. Polym. Sci.* **2003,** *87*, 2216.

19. López-Manchado, M. A.; Arroyo, M.; Herrero, B.; Biagiotti, J. J. *Appl. Polym. Sci.* **2003,** *89*, 1.

20. Das, A.; Stockelhuber, K. W.; Jurk, R.; Jehnichen, D.; Heinrich, G. *Appl. Clay Sci.* **2011,** *51*, 117.

21. Liu, Q.; Zhang, Y.; Xu, H. *Appl. Clay Sci.* **2008,** *42*, 232.

22. Sadhu, S.; Bhowmick, A. K. J. *Appl. Polym. Sci.* **2004,** *92*, 698.

23. Sharif, J.; Yunus, W. M. *Z.W.; Dahlan, K.Z. Hj. M.; Ahmad, M.H. Polym. Test* **2005,** *24*, 211.

24. Samyn, F.; Bourbigot, S.; Jama, C.; Bellayer, S.; Nazare, S.; Hull, R.; Castrovinci, A.; Fina, A.; Camino, G. *Eur. Polym. J.* **2008,** *44*, 1642.

25. Bafna, A.; Beaucage, G.; Mirabella, F.; Mehta, S. *Polymer* **2003,** *44*, 1103.

26. Gu, Z.; Song, G.; Liu, W.; Yang, S.; Gao, J. *Clays Clay Miner.* **2010,** *58*, 72.

27. Carli, L. N.; Roncato, C. R.; Zanchet, A.; Mauler, R. S.; Giovanela, M.; Brandalise, R. N.; Crespo, J. S. *Appl. Clay Sci.* **2011,** *52*, 56.

28. Ali, Z.; Le, H. H.; Ilisch, S.; Busse, K.; Radusch, H.-J.J. *Appl. Polym. Sci.* **2009,** *113*, 667.

29. Varghese, S.; Karger-Kocsis, J. J. *Appl. Polym. Sci.* **2004,** *91*, 813.

30. Chattopadhyay, P. K.; Chattopadhyay, S.; Das, N. C.; Bandyopadhyay, P. P. *Mater. Des.* **2011,** *32*, 4696.

31. Nie, Y.; Qu, L.; Huang, G.; Wang, B.; Weng, G.; Wu, J. *Polym. Adv. Technol.* **2012,** *23*, 85.

32. Nie, Y.; Huang, G.; Qu, L.; Wang, X.; Weng, G.; Wu, J. *Polymer* **2011,** *52*, 3234.

33. Jankovič, Ľ.; Madejová, J.; Komadel, P.; Jochec-Mošková, D.; Chodák, I. *Appl. Clay Sci.* **2011,** *51*, 438.

34. Madejová, J.; Jankovič, Ľ.; Pentrák, M.; Komadel, P. *Vibr. Spect.* **2011,** *57*, 8.